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(54) Title: HYDROFORMYLATION METHOD FOR MAKING ALDEHYDES FROM STERICALLY HINDERED OLEFINS

(57) Abstract: A process for preparing an aldehyde includes contacting a mixture of C<sub>6</sub>-C<sub>12</sub> olefins from a refinery olefinic material, hydrogen, carbon monoxide, and a hydroformylation catalyst under hydroformylation reaction conditions wherein the catalyst includes a Group VIII metal and an effective amount of a ligand selected from triarylphosphites, sterically hindered tri-organophosphites containing at least one aryl group and fluorophosphites.

**HYDROFORMYLATION METHOD FOR MAKING ALDEHYDES  
FROM STERICALLY HINDERED OLEFINS**

**BACKGROUND OF THE INVENTION**

**5 Field of the Invention**

The present invention relates to hydroformylation of certain sterically hindered olefins to produce aldehydes. Particularly, the present invention relates to solubilized rhodium phosphite complex catalyzed hydroformylation of specific sterically hindered olefins to produce aldehydes. More particularly, the present invention relates to a 10 hydroformylation process for preparing aldehydes from C<sub>6</sub>-C<sub>12</sub> sterically hindered olefins using a rhodium containing catalyst and a triorganophosphite ligand and particularly triarylphosphite ligands.

**Background of the Invention**

Various lower olefinic stocks are available from petroleum sources and many 15 procedures are known for converting lower olefins to higher olefins or higher molecular weight compounds. Such processes include catalytic dimerization for converting propylene and butenes to heptenes and octenes, hydroformylation of the olefins to aldehydes, aldol processes for converting lower aldehydes to higher aldehydes and hydrogenation for converting the aldehydes to alcohols. A process generally known as 20 the "Polygas" process is well known in the art for converting refinery grade propylene into isomeric mixtures of hexene and nonene, which are valuable feedstocks for hydroformylation.

The hydroformylation process, also known as the oxo process, involves the oxygenating an olefinic feedstock to produce an aldehyde having one carbon atom 25 greater than the mono-olefin feedstock. For sterically hindered olefins, the process typically includes contacting the olefinic feedstock with carbon monoxide and hydrogen in the presence of a catalyst, typically at an operating pressure greater than about 400 psi and a temperature greater than about 120°C. The most extensive use of the oxo process is for preparing normal- and iso-butyraldehyde from propylene. The ratio of normal

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aldehyde product to the iso aldehyde product typically is referred to as the normal to iso (N:I) or the normal to branched (N:B) ratio. In the case of propylene, the normal- and iso-butyraldehydes obtained from propylene are in turn converted into many commercially-valuable chemical products such as, for example, n-butanol, 2-ethyl-  
5 hexanol, n-butyric acid, isobutanol, neopentyl glycol, 2,2,4-trimethyl-1,3-pentanediol, the mono-isobutyrate and di-isobutyrate esters of 2,2,4-trimethyl-1,3-pentanediol. The hydroformylation of higher  $\alpha$ -olefins such as 1-octene, 1-hexene and 1-decene yield aldehyde products which are useful feedstocks for the preparation of detergent alcohols and plasticizer alcohols.

10 U.S. Patent No. 4,518,809 discloses a process for converting propylene to C<sub>14</sub> alcohols using dimerization, oxo, aldol and hydrogenation processes. The process involves conducting an oxo reaction with a hexene mixture composed mainly of methyl pentenes, as produced by dimerization of propylene, and a cobalt catalyst to obtain a heptanal product in which carbonylation has occurred primarily on the terminal carbon  
15 and then conducting an aldol reaction of the heptanal product to obtain C<sub>14</sub> alcohols. The patent further discloses that the cobalt catalyst produces a relatively high ratio of aldehydes without 2-branching, as is necessary for aldol reactions to give a good yield of aldol product. The oxo reaction is operated under pressures of from 500 psig to 5000 psig.

20 U.S. Patent No. 4,263,449 discloses a process for producing an alcohol by hydroformylation of an olefin in a substantially water immiscible solvent and in the presence of a hydroformylation catalyst which is soluble in the solvent. Water is added to the reaction mixture at a ratio of from 0.5 to 30 times the amount, by weight, of the resulting aldehyde. The product is then hydrogenated in the presence of a hydrogenation  
25 catalyst. The resulting product is separated by phase separation. The intermediate aldehyde is not separated prior to hydrogenation. The hydroformylation catalyst used is HRh(CO)(PR<sub>3</sub>)<sub>3</sub> or HRh(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> where the PR<sub>3</sub> moiety is an organic tertiary phosphine and R is a C<sub>2</sub>-C<sub>20</sub> alkyl group or C<sub>6</sub>-C<sub>20</sub> aryl group.

U.S. Patent No. 4,599,206 discloses the use of diorganophosphite ligands in Group  
30 VIII transition metal complex catalyzed carbonylation processes.

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U.S. Patent No. 4,426,542 discloses a process for converting butenes to C<sub>10</sub> plasticizer alcohols having at least 80-90 % 2-propylheptanol using an oxo reaction of the butenes to obtain amyl aldehydes followed by an aldol reaction of the aldehydes under conditions to cause the n-pentanal to react but with incomplete conversion of branched 5 aldehydes. The process further includes hydrogenating the product to produce alcohols. The oxo stage of the process is conducted under usual conditions pertaining to cobalt catalyzed hydroformylation reactions, i.e., pressures from 1000 psig to 5000 psig.

U.S. Patent Nos. 3,527,809 and 3,917,661 disclose an oxo process having high normal to iso isomer ratios for α-olefin feedstock and using a rhodium containing 10 complex in the presence of tertiary organo-containing ligands containing a trivalent atom of Group VA including phosphorus, arsenic and antimony. Such ligands includes trialkylphosphites and triarylphosphites.

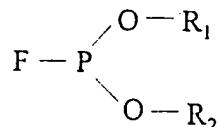
Although the art discloses the hydroformylation of lower α-olefins, such as propylene and 1-butene, for making aldehydes as well as making higher molecular 15 weight aldehydes via the aldol process, there is a need for preparing aldehydes, without extra process steps, such as aldol condensation, directly from higher olefinic feedstocks and particularly refinery olefins that have internal olefin and skeletal carbon branching within the olefin. Moreover, there is a need to be able to efficiently hydroformylate, at reaction pressures below 400 psig, mixtures of olefins where the ratio of α (alpha) olefins 20 to the sum of branched chain and internal olefins is less than about 3/1.

#### SUMMARY OF THE INVENTION

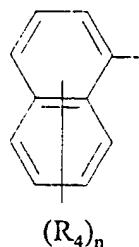
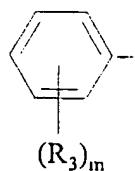
It has now been discovered that sterically hindered olefins and particularly sterically hindered C<sub>6</sub>-C<sub>12</sub> olefins from refinery olefinic feedstock having low alpha 25 olefin content and large amounts of skeletal carbon branching and particularly where the ratio of alpha olefins to the sum of branched chain and internal olefins is less than about 3/1, are capable of hydroformylation, i.e., aldehyde formation, via hydroformylation using a group VIII transition metal containing catalyst and an effective amount of a ligand selected from a triarylphosphite, sterically hindered tri-organophosphites 30 containing at least one aryl group and fluorophosphites.

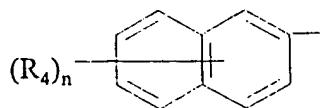
## DETAILED DESCRIPTION OF THE INVENTION

In general such hydroformylation reactions of the present invention involve the production of aldehydes by reacting an olefinic unsaturated compound with carbon monoxide and hydrogen in the presence of a solubilized Group VIII transition metal-phosphite complex catalyst in a liquid medium that may contain a solvent for the catalyst, and free phosphite ligand, i.e. ligand that is not complexed with the Group VIII metal in the active complex catalyst. Desirably, the catalysts which are contemplated consist of rhodium in complex combination with an effective amount of a ligand containing trivalent atom of a Group VA element which preferably is phosphorous. More preferably, the ligand is selected from a fluorophosphite or triarylphosphite a compound.



wherein R<sub>1</sub> and R<sub>2</sub> are independently selected from alkyl of up to 8 carbon atoms, benzyl,  
15 cyclopentyl, cyclohexyl, cycloheptyl or an aryl group having the formula:





and wherein R<sub>3</sub> and R<sub>4</sub> are independently selected from alkyl, alkoxy, halogen, cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl, carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate salts in which the  
 5 alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxycarbonyl and alkanoyloxy groups contains up to 8 carbon atoms; m and n independently are 0, 1 or 2. The total carbon atom content of the hydrocarbyl radicals represented by R<sub>1</sub> and R<sub>2</sub> is from 2 to 35. The R<sub>1</sub> and R<sub>2</sub> groups may also be bound to each other by a carbon atom to carbon atom bridge linkage, whereby the R<sub>1</sub> and R<sub>2</sub> groups may be connected together by 0, 1, or 2  
 10 carbon atoms linked between the two R groups. More preferably, the fluorophosphite is 2,2'-ethylidenebis(4,6-di-tert-butylphenyl)fluorophosphite. Desirably, the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is about 1:1 to 70:1. Such fluorophosphite ligands are described in greater detail in U.S. Patent No. 5,840,647, the disclosure of which is incorporated herein by reference.

15 The triarylphosphite ligands and certain sterically hindered triorgano-phosphites incorporating at least one aryl group represent the preferred class of ligands. Suitable examples of such include triphenylphosphite, trinaphthylphosphite, tri(p-methoxyphenyl)phosphite, bis(2,4-di-tert-butylphenyl) pentaerithyritol diphosphite, (2,4,6-tri-tert-butylphenyl)-2-butyl-2-ethyl-1,3-propanediol phosphite, tetra(2,4-di-tert-  
 20 butyl)biphenylene diphosphite and phenyl neopentylglycol phosphite. The preferred triarylphosphite ligand is tris(2,4-di-tert-butylphenyl)phosphite.

The Group VIII metals of the catalyst compound may be provided in the form of various metal compounds such as carboxylate salts of the transition metal. Desirably the Group VIII metal is rhodium. Rhodium compounds that may be used as a source of the  
 25 rhodium for the active catalyst include rhodium II or rhodium III salts of carboxylic acids. For example, suitable materials include di-rhodium tetraacetate dihydrate, rhodium(II) acetate, rhodium(II) isobutyrate, rhodium(II) 2-ethylhexanoate, rhodium(II) benzoate and rhodium(II) octanoate. Also, rhodium carbonyl species such as Rh<sub>4</sub>(CO)<sub>12</sub>, Rh<sub>6</sub>(CO)<sub>16</sub> and rhodium(I) acetylacetonate dicarbonyl may be suitable rhodium feeds.

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Less desirable rhodium sources are rhodium salts of strong mineral acids such as chlorides, bromides, nitrates, sulfates, and phosphates.

- The concentration of the rhodium and ligand in the hydroformylation reaction mixture is not critical for the production of oxygenated hydrocarbons in accordance with 5 the present invention. The concentration of rhodium in the reaction mixture may vary from 1 mg/liter up to 5000 mg/liter or more. When the process is operated within the practical conditions of this invention, the concentration of rhodium in the reaction solution is in the range of about 20 to about 1000 mg/liter, preferably from about 20 to about 500 mg/liter and most preferably from about 20 to about 300 mg/liter.
- 10 Concentrations of rhodium lower than this range generally do not yield acceptable reaction rates with most olefin reactants and/or require reactor operating temperatures that are so high as to be detrimental to catalyst stability.

- The ratio of gram moles of ligand to the gram atoms of the transition metal can vary over a wide range, e.g., gram mole ligand:gram atom transition metal ratios of about 15 1:1 to 200:1. For the rhodium-containing catalyst systems the gram mole ligand:gram atom rhodium ratio preferably is in the range of about 1:1 up to 70:1 with ratios in the range of about 1:1 to 12:1 being particularly preferred. A gram mole ligand:gram atom rhodium ratio of at least 1:1 normally is maintained in the reaction mixture.
- Concentrations of rhodium lower than this range generally do not yield acceptable 20 reaction rates with most olefin reactants and/or require reactor operating temperatures that are so high as to be detrimental to catalyst stability.

- Solvents are not required in the practice of the invention but often times their use is desirable and practical. Normally liquid, organic solvents which are inert or which do not interfere to any substantial degree with the desired hydroformylation reaction under 25 the operative conditions employed are acceptable. Such compounds and materials include various alkanes, cycloalkanes, alkenes, cycloalkenes, carbocyclic aromatic compounds, alcohols, esters, ketones, acetals, ethers and water. Specific examples of such solvents include alkane and cycloalkanes such as dodecane, decalin, octane, iso-octane mixtures, cyclohexane, cyclooctane, cyclododecane, methylcyclohexane; aromatic hydrocarbons 30 such as benzene, toluene, xylene isomers, tetralin, cumene, alkyl-substituted aromatic compounds such as the isomers of diisopropylbenzene, triisopropylbenzene and tert-

butylbenzene. Additionally, reactant alkenes and cycloalkenes such as 1,7-octadiene, dicyclopentadiene, 1,5-cyclooctadiene, octene-1, octene-2, 4-vinylcyclohexene, cyclohexene, 1,5,9-cyclododecatriene, 1-pentene and the like may be used as solvents. Other examples of suitable solvents include: crude hydrocarbon mixtures such as

5 naphtha; mineral oils and kerosene; high-boiling esters such as 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. The aldehyde product of the hydroformylation process also may be used. In practice, the preferred solvent is the higher boiling by-products that are naturally formed during the process of the hydroformylation reaction and the subsequent steps, e.g., distillations, that are required for aldehyde product isolation. The main

10 criteria for the solvent is that it dissolves the catalyst and olefin feedstock and does not act as a poison to the catalyst. Accordingly, recycle olefins in combination with fresh olefin reactor feed is a suitable solvent. Preferred solvents for the production of aldehydes are those that have a sufficiently high boiling point to remain, for the most part, in a gas sparged reactor. Solvents and solvent combinations that are preferred for

15 use in the production of less volatile and non-volatile aldehyde products include 1-methyl-2-pyrrolidinone, dimethyl-formamide, perfluorinated solvents such as perfluorokerosene, sulfolane, water, and high boiling hydrocarbon liquids as well as combinations of these solvents. It has been found that non-hydroxylic compounds, in general, and hydrocarbons, in particular, may be used advantageously as the hydroformylation solvent

20 since their use can minimize decomposition of the fluorophosphite ester ligands.

No special or unusual techniques are required for preparing the catalyst systems and solutions of the present invention, although it is preferred, to obtain a catalyst of high activity, that all manipulations of the rhodium and fluorophosphite ligand components be carried out under an inert atmosphere, e.g., nitrogen, argon and the like. The desired

25 quantities of a suitable rhodium compound and ligand are charged to the reactor in a suitable solvent. The sequence in which the various catalyst components or reactants are charged to the reactor is not critical.

A desirable and unique feature of the present invention is the low operating pressure of the hydroformylation process. Acceptable total pressures of carbon

30 monoxide and hydrogen for the process range from about atmospheric to less than about 450 psig. Desirably, total pressures range from atmospheric to about 350 psig and

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preferably less than about 300 psig. In the hydroformylation process the molar ratio of hydrogen to carbon monoxide in the reactor can be varied and is generally selected depending upon the operating parameters of the reaction system. Typically, however, such hydrogen:carbon monoxide ratios are from 1:10 to 10:1.

5        The process may be carried out at temperatures in the range of about 20° to 200°C. Preferred hydroformylation reaction temperatures are from about 50°C to about 135°C, and more preferred temperatures range from about 75° to about 125°C. Higher reactor temperatures are not favored because of increased rates of catalyst decomposition while lower reactor temperatures result in relatively slow reaction rates.

10      The olefins that may be hydroformylated by means of our novel process comprise aliphatic, including ethylenically-unsaturated, refinery distillation cuts which will contain a mixture of olefins over a range of several carbon numbers, preferably in the range of C<sub>6</sub> through C<sub>12</sub> and desirably have from 75 mole % to about 100 mole % unsaturated hydrocarbons. The alpha olefin content of the feedstock can be less than about 40 mole 15 %, as little as less than about 5 mole % or contain essentially 0 mole % alpha olefins, i.e. where all the detectable olefins in the mixture may be internal olefins or have at least one carbon-skeletal branch. The present invention is particularly useful in the hydroformylation of refinery olefins, such as those derived from Polygas or Dimersol as olefin mixtures. Depending on the hydrocarbonaceous feedstocks and the degree of 20 refining, these olefins may consist of predominantly one carbon number fraction, or may cover a range of different molecular weights.

In most hydroformylation processes, feeds with high alpha-olefin contents are preferred. With some catalysts, substantially linear olefins with lower alpha-olefin contents, are acceptable feedstocks. An advantage of the present invention is the ability 25 to use refinery olefins containing very little alpha-olefin and which have high amounts of skeletal carbon branching. Unexpectedly, it has been found that the catalysts described in this invention are effective with olefin mixtures that contain little, or no alpha-olefin. These catalysts are effective with olefin mixtures that may contain a high level of highly branched components. The refinery olefins are economically advantaged as feeds for 30 hydroformylation, when compared to pure alpha-olefins or olefin mixtures that are predominantly linear.

One skilled in the art will understand that the catalyst and ligand system can also be used for hydroformylation of such olefinic feedstocks having ethylenically-unsaturated, low molecular weight polymers, such as poly-butadiene, alicyclic, aromatic and heterocyclic mono-, di- and tri-olefins containing up to about 40 carbon atoms.

- 5 Examples of aliphatic olefins that may be utilized include straight and branched, unsubstituted and substituted, aliphatic mono- $\alpha$ -olefins containing up to about 20 carbon atoms. Aliphatic di-olefins may contain up to about 40 carbon atoms. Examples of the groups that may be present on the substituted mono- $\alpha$ -olefins include hydroxy; alkoxy including ethers and acetals; alkanoyloxy such as acetoxy; amino including substituted
- 10 amino; carboxy; alkoxycarbonyl; carboxamido; keto; and cyano.

The cyclic olefins which may be used in the hydroformylation process of the present invention may be cycloalkenes, e.g., cyclohexene, 1,5-cyclooctadiene, and cyclodecatriene, and from various vinyl-substituted cycloalkanes, cycloalkenes, heterocyclic and aromatic compounds. Examples of such cyclic olefins include 4-vinylcyclohexene, 1,4-cyclohexadiene, 4-cyclohexene-carboxylic acid, methyl 4-cyclohexene-carboxylic acid, 1,4-cyclooctadiene and 1,5,9-cyclododecatriene.

- 15 Any of the known hydroformylation reactor designs or configurations may be used in carrying out the process provided by the present invention. For example, a gas-sparged, vapor take-off reactor design may be used. Typically, in this mode of operation, the catalyst which is dissolved in a high boiling organic solvent under pressure does not leave the reaction zone and the aldehyde product taken overhead by the unreacted gases. The overhead gases are chilled in a vapor/liquid separator to condense and/or collect the aldehyde product and the gases can be recycled to the reactor. The liquid product is let down to atmospheric pressure for separation and purification using conventional techniques known to those skilled in the separation art. The process also may be practiced in a batchwise manner using an autoclave and contacting the olefin, hydrogen and carbon monoxide with the catalyst and ligand described herein and under hydroformylation conditions.
- 20
- 25

- 30 Another acceptable hydroformylation reactor design is a liquid overflow where catalyst and feedstock are pumped into a reactor and are allowed to overflow with product aldehyde. The aldehyde product may be separated from the catalyst by

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conventional means such as by distillation or extraction. The catalyst is then recycled back to the reactor. Alternatively, two or more liquid overflow reactors may be used in series to give high conversions of the olefin feedstock.

Advantageously, the aldehydes made by the process of the present invention can be  
5 hydrogenated to form alcohols, which may be converted to useful plasticizers such as diisoheptylphthalate or diisodecylphthalate and the like. The aldehydes made may further be oxidized using an appropriate oxygenation source, such as air, to form the corresponding carboxylic acids. A particular advantage of the catalyst of the present invention is the production of aldehydes having minimal carbon branching on the carbon  
10 atom alpha to the aldehyde group using low pressure hydroformylation conditions. The corresponding alcohol derivatives are particularly desirable for plasticizer applications due to their greater reactivity to form plasticizer esters.

The present invention is further illustrated by the following example.

A catalytic solution was prepared under nitrogen using 0.52 grams (1.0 mmol) of  
15 dicarbonylacetylacetonato rhodium (I) (available from Strem Chemicals, Newburyport, MA, ACS number 14874-82-9), 4.6 grams (5mmole) of tris(2,4-di-t-butyl) phosphite (Tradename Irgafos 168 available from Ciba-Geigy Corporation or Ultrinox 668 available from General Electric Specialty Chemicals) and 125 mL of polygas nonene having 99.6% olefin content and a bromine number (as per ASTM 1159) of 148 as a  
20 solvent. The catalytic solution was warmed to assure all components dissolved. The catalytic solution was charged to a 1.0 L stainless steel Parr Series 4520 mini-reactor equipped with a magnetic drive and gas entrainment impeller along with another 525mL of the polygas nonene and 20 mL n-heptane, as internal standard. The reactor was loaded and unloaded in a glove box.

25 The reactor was sealed and pressurized to 300 psig using a 1:1 premixture of hydrogen and carbon monoxide (syngas). The reactor was heated to 120°C and maintained between 300-400 psi by adding syngas. After 6.2 hours, the supply of syngas was stopped, stirring ceased, the reactor was cooled and vented. Gas chromatography of the recovered liquid revealed that 69.4 mol % of the product had been converted to a  
30 mixture of decyl aldehydes. The ratio of aldehyde product having no carbon branching

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on the alpha carbon to aldehyde product having carbon branching on the alpha carbon of the product was 1.6.

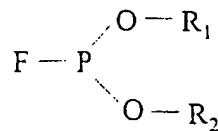
Having described the invention in detail, those skilled in the art will appreciate that modifications may be made to the various aspects of the invention without departing 5 from the scope and spirit disclosed and described herein. It is, therefore, not intended that the scope of the invention be limited to the specific embodiments illustrated and described but rather it is intended that the scope of the present invention be determined by the appended claims and their equivalents.

## CLAIMS

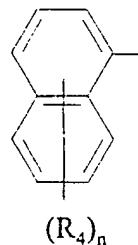
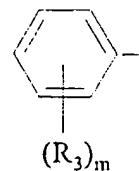
What is claimed is:

1. A process for preparing an aldehyde comprising contacting under hydroformylation reaction conditions a refinery olefinic feed stock having a mixture of C<sub>6</sub>-C<sub>12</sub> olefins, hydrogen, carbon monoxide, and a hydroformylation catalyst wherein said catalyst includes a group VIII metal and an effective amount of a ligand selected from the group consisting of triarylphosphite, sterically hindered triorganophosphites containing at least one aryl group and fluorophosphite.
5. The process of claim 1 wherein said hydroformylation reaction conditions have a pressure of less than 350 psig and a temperature of less than about 150°C.
10. The process of claim 2 wherein said hydroformylation reaction conditions have a pressure of from atmospheric to less than about 300 psig and a temperature of less than about 140°C.
15. The process of claim 1 wherein said mixture of C<sub>6</sub>-C<sub>12</sub> olefins is sterically hindered and have an alpha-olefin content of less than about 40 mol%.
5. The process of claim 4 wherein said group VIII metal is rhodium.
6. The process of claim 5 wherein said rhodium has a concentration of from about 20 to about 1000 mg per liter.
7. The process of claim 6 wherein said concentration is from about 20 to 500 mg per liter.
20. The process of claim 6 wherein said concentration is from about 20 to 300 mg per liter.
8. The process of claim 1 wherein said triarylphosphite ligand is selected from the group consisting of triphenylphosphite, trinaphthylphosphite, tri(p-methoxyphenyl)phosphite, tetra(2,4-di-tert-butyl)biphenylene diphosphite, and tris(2,4-di-tert-butylphenyl)phosphite.
25. The process of claim 1 wherein said triarylphosphite ligand is tris(2,4-di-tert-butylphenyl)phosphite.
10. The process of claim 1 wherein said triarylphosphite ligand is tris(2,4-di-tert-butylphenyl)phosphite.
11. The process of claim 1 wherein said fluorophosphite has the general formula:

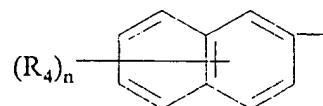
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wherein R<sub>1</sub> and R<sub>2</sub> are independently selected from alkyl of up to 8 carbon atoms,  
 5       benzyl, cyclopentyl, cyclohexyl, cycloheptyl or an aryl group having the formula:



10



wherein R<sub>3</sub> and R<sub>4</sub> are independently selected from alkyl, alkoxy, halogen,  
 15       cycloalkoxy, formyl, alkanoyl, cycloalkyl, aryl, aryloxy, aroyl, carboxyl,  
          carboxylate salts, alkoxycarbonyl, alkanoyloxy, cyano, sulfonic acid and sulfonate  
          salts in which the alkyl moiety of such alkyl, alkoxy, alkanoyl, alkoxycarbonyl and

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alkanoyloxy groups contains up to 8 carbon atoms; m and n independently are 0, 1 or 2; and the total carbon atom content of the hydrocarbyl radicals represented by R<sub>1</sub> and R<sub>2</sub> is from 2 to 35 and wherein the ratio of gram moles fluorophosphite ligand to gram atoms rhodium is about 1:1 to 70:1.

- 5 12. The process of claim 11 wherein R<sub>1</sub> and R<sub>2</sub> are bound to each other by a carbon atom bridge linkage connected by 0, 1, or 2 carbon atoms linked between R<sub>1</sub> and R<sub>2</sub>.
13. The process of claim 12 wherein said fluorophosphite is 2,2'-ethyldenebis(4,6-di-tert-butylphenyl)fluorophosphite.
- 10 14. The process of claim 1 wherein said sterically hindered triorganophosphite ligands having at least one aryl group are selected from the group consisting of (2,4,6-tri-tert-butylphenyl)-2-butyl-2-ethyl-1,3-propanediol phosphite, bis(2,4-di-tert-butylphenyl)pentaerithyrtol diphosphite and phenyl neopentylglycol phosphite.
15. A process for preparing an aldehyde comprising contacting under hydroformylation reaction conditions a refinery olefinic feed stock having a mixture of C<sub>6</sub>-C<sub>12</sub> olefins, hydrogen, carbon monoxide, a catalyst and a hydroformylation solvent, wherein said catalyst includes from 20 to 1000 mg per liter rhodium and an effective amount of a ligand selected from a triarylphosphite.
- 20 16. The process of claim 15 wherein said mixture of C<sub>6</sub>-C<sub>12</sub> olefins are sterically hindered and have less than 40 mol% alpha-olefin content.
17. The process of claim 15 wherein said triarylphosphites ligand is tris(2,4-di-tert-butylphenyl)phosphite.
18. The process of claim 15 wherein said rhodium concentration is from about 20 to 300 mg per liter.
- 25 19. The process of claim 15 wherein said mixture of C<sub>6</sub>-C<sub>12</sub> olefins are sterically hindered and have less than about 5 mol% alpha-olefin content.
20. The process of claim 15 wherein said mixture of C<sub>6</sub>-C<sub>12</sub> olefins are sterically hindered and are essentially free of alpha-olefin content.

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21. A process for preparing an aldehyde comprising contacting under hydroformylation reaction conditions a refinery olefinic feed stock having a mixture of C<sub>6</sub>-C<sub>12</sub> olefins, hydrogen, carbon monoxide, and a catalyst, wherein said catalyst includes from 20 to 500 mg per liter rhodium and an effective amount of tris(2,4-di-tert-butylphenyl)phosphite.
- 5 22. The process of claim 21 wherein from about 1:1 to 200:1 gram mole ligand:gram atom transition metal is present in said catalyst.
23. The process of claim 21 wherein from about 1:1 to 70:1 gram mole ligand:gram atom transition metal is present in said catalyst.
- 10 24. The process of claim 21 wherein from about 1:1 to 12:1 gram mole ligand:gram atom transition metal is present in said catalyst.
25. The process of claim 21 wherein said process is carried out at a pressure of less than about 350 psig, a temperature of from about 75° to about 125°C and a hydrogen to carbon monoxide mole ratio of from 1:10 to 10:1.

# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/US 01/00135

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C07C45/50

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 527 809 A (PRUETT ROY L ET AL) 8 September 1970 (1970-09-08) cited in the application examples 8-19,22-33,39-43,45-50,59,61-65,67-74 ---	1-3,5-9
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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\*&\* document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**

In .ational Application No

PCT/US 01/00135

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

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X	EP 0 518 241 A (MITSUBISHI CHEM IND) 16 December 1992 (1992-12-16) examples 1-7,11-17,20,22 ---	1,4-8, 14-16,18
X	EP 0 503 564 A (MITSUBISHI CHEM IND) 16 September 1992 (1992-09-16) comparative example 1 ---	1,4-10, 14-22
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